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Synthesis of the mineral geikielite $MgTiO_3$

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The preparation of pure geikielite, $MgTiO_3$, is carried out by precipitation with NaOH solution at pH ~ 12 from solutions Ti^{4+}/Mg^{2+} in molar ratio 1/1 M and calcination of the precipitate at 600 °C in a dynamic atmosphere: heating rate 300 °C h^{-1}.

At room temperature and a 1 KHz of frequency the dielectric constant (ε) and the electric resistivity (ρ) were measured. The values were $\varepsilon = 15.0$ and $\rho = 1.1 \times 10^{10}\ \Omega\ cm^{-1}$.

1. Introduction

The mineral of titanium and magnesium that exists most frequently in the nature is the metatitanate $MgTiO_3$, geikielite. Its structure is of the type ilmenite with rhombohedral mesh.

The metatitanate $MgTiO_3$, has many industrial applications: in dew sensors [1]; in pigments for protective coatings, with good water, weathering and impact resistance [2]; in the composition of binders by increasing the flexural strength [3] and, principally, for their dielectric properties, in chip capacitors, high frequency capacitors and temperature–compensating capacitors.

Therefore, the synthesis of the titanate has been the subject of several different papers. In the majority of these, the preparation of the titanate was carried out by solid state reaction at a high temperature between the titanium oxide and different magnesium salts.

According to Brusset *et al.* [4] the first synthesis of the geikielite was that of Hautefeuille in 1864, which was obtained from a mixture of magnesium chloride, ammonium chloride and titanium oxide by calcination at 900 °C.

Naylor and Cook [5] obtained the $MgTiO_3$ from a stoichiometric mixture of $MgO + TiO_2$ (through two successive calcinations in a vacuum) for 11 hours at 1300–1350 °C. In 1948, Wyss [6] studied the influence of temperature and heating time on the abovementioned reaction. From mixtures of anhydrous or hydrated TiO_2 with $MgCO_3$ by heating at 900–1100 °C, Tanaka [7], Nutting [8] and Turlier [9] prepared the $MgTiO_3$, while Rassudova *et al.* [10] prepared it by adding magnesium chloride to a mixture of titanium hydroxide and magnesium hydroxycarbonate and heating at 850 °C for 2 hours.

Recently, new methods of obtaining the geikielite by decreasing the reaction temperature and increasing the stoichiometric value and the purity of the particles have been employed: decomposition of a tartaric complex of titanium and magnesium by Saikali *et al.* [11]; coprecipitation of oxalates by Kudienko and Trosheva [12] and of citrates by Mulder [13]. On the other hand, Shvets *et al.* [14] obtained a synthetic geikielite from stoichiometric mixtures of TiO_2 and MgO at 550 °C and 1×10^8 Pa in hydrothermal conditions.

In this paper we give a method for synthesis of the geikielite by coprecipitation of the system Ti^{4+}–Mg^{2+} in molar ratio 1/1. The precipitating agent was an aqueous solution of sodium hydroxide.

2. Experimental procedure

2.1. Products

Titanium fine powder, $MgSO_4.7H_2O$, H_2SO_4 95–97% and NaOH were from Merck a.r. quality.

2.2. Preparation of the samples

The sulphuric solutions of Ti^{4+}/Mg^{2+} 1/1 M were prepared as follows: A titanium fine powder was weighed and boiled with 2N H_2SO_4 and a few drops of concentrated nitric acid until dissolved. To this solution, the necessary sample amount of $MgSO_4.7H_2O$ was added.

The sulphuric solutions of titanium and magnesium, strongly acid, were precipitated by adding, drop by drop, a concentrated aqueous solution of sodium hydroxide. The solution was stirred quickly during the addition of sodium hydroxide and the pH controlled using a pH meter.

The gelatinous white precipitates were filtered through a No. 4 coarse filter.

In the filtrates we analysed the titanium spectrophotometrically with 2% cromotropic acid and magnesium by complexometric titration with EDTA using Eriochrome Black T as an indicator. Both analyses were negative in all the samples, showing that the precipitations were quantitative and that the titanium-magnesium composition of the precipitates were also 1/1 M.

The precipitates were washed with cold distilled water until the sulphates ions were removed. By Atomic Absorption we show that the washed precipitates were free of sodium ions.

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In the washed waters which we analysed for Ti^{4+} and Mg^{2+}, the result was also negative indicating that the precipitates did not dissolve during the washing. The precipitates were dried at room temperature, ground (grain size less than 95 μm) and kept in closed vessels.

2.3. Apparatus

Thermogravimetry: A Mettler TA3000 thermobalance was used, heating rate 10 K min^{-1}.

Differential thermal analysis: A homemade system using a vertical furnace and a temperature regulation system, both from Adamel, was used. A differential chromel–alumel thermopar was used, heating rate 5 K min^{-1}.

X-ray powder diffraction: A Philips PW 1130 diffractometer was used, with a Ni filter and Cu kα, radiation.

Infrared spectroscopy: A Perkin Elmer mod. 683 was used. The samples were prepared as mulls using fluorolube as a mulling agent for the region 4000–1500 cm^{-1}, and KBr pellets for the region 1500–200 cm^{-1}.

Scanning electron microscopy: A Jeol JST9 35C instrument was used with an energy dispersive spectrometer (Kevex 7077). The samples were metallized with gold by sputtering.

3. Results and discussion

The X-ray diagrams of the precipitates Ti^{4+}/Mg^{2+} 1/1 M (Fig. 1a) indicated that precipitates were practically amorphous and we could only see an incipient order of the planes of the brucite, $Mg(OH)_2$. In Fig. 2a we give the i.r. spectra of the precipitate. The spectrum displayed the following bands: a sharp band at 3700 cm^{-1} due to the stretching vibrations of the hydroxyl groups; a wide band at 3400 cm^{-1} associated with the stretching vibrations of the crystallization water; a band at 1640 cm^{-1} due to CO_3^-, which indicated that the precipitate absorbs a little carbonic from the air. Between 1000 and 200 cm^{-1}, a strong band exists at 540 cm^{-1} due to metal–oxygen vibrations.

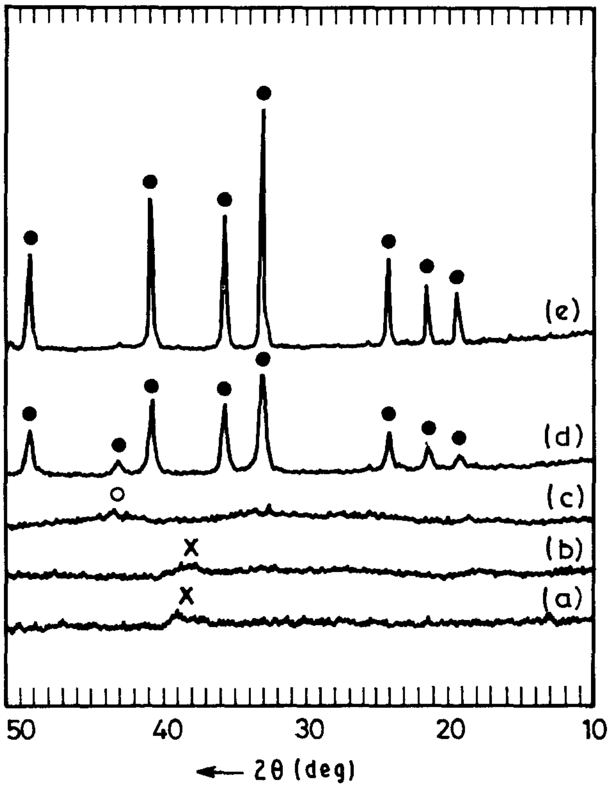

Figure 1 X-ray diagrams of the precipitate. (×) $Mg(OH)_2$: (○) MgO: (●) $MgTiO_3$ (a) room temperature-dried; (b) 300 °C; (c) 460 °C; (d) 660 °C; (e) 1000 °C.

In Fig. 3 we give the TG and DTG curves. The TG curve shows only one loss from the very beginning until 650 °C, with two inflexion points at 240 °C and at 380 °C, respectively. The total weight loss was 43.0% with respect to the initial weight or 75% with respect to the residuum weight (TiO_2 + MgO). In the DTG curve there are two peaks with Tp = 110 °C and 375 °C. The position of both peaks permitted us to attribute the first loss to dehydration water and the second one to dehydroxylation water. This second loss represented 10% of the residuum weight. But if all the

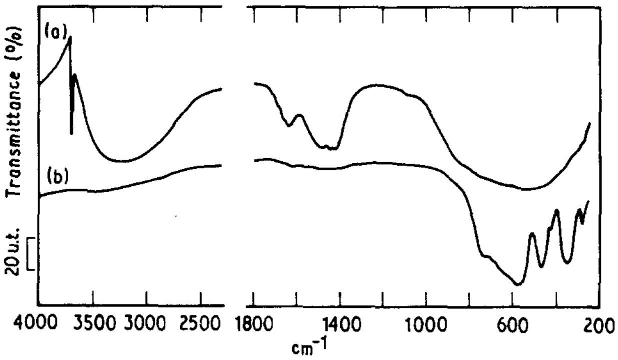

Figure 2 IR spectra of the precipitate (a) room temperature-dried; (b) 660 °C.

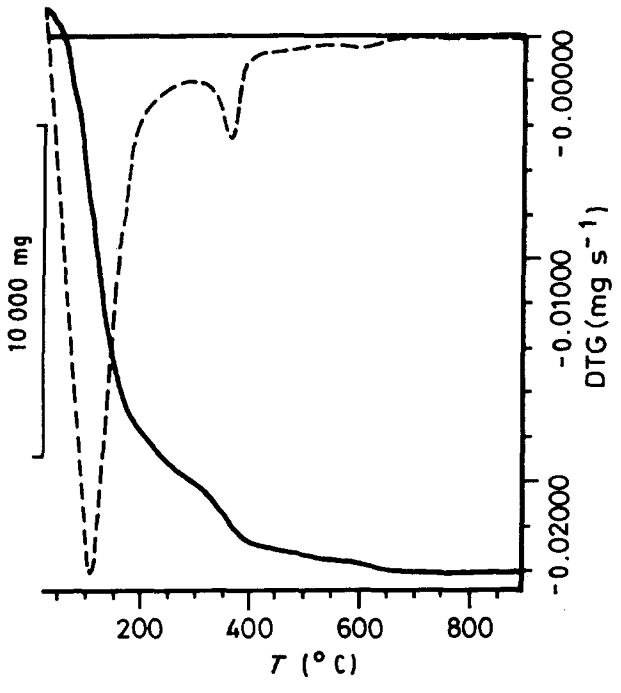

Figure 3 TG and DTG curves of the precipitate, sample weight: 39.198 mg.

magnesium of the sample was converted to magnesium hydroxide the loss would correspond to 15%.

From the results mentioned above, we can deduce that the titanium in its precipitation carried away some of the magnesium present in the solution and the rest of it precipitated as $Mg(OH)_2$ from pH 7–8, until pH 12. The precipitation of titanium is complete at pH 7–8.

The magnesium that coprecipitates with titanium has two effects on the titanium oxide formed: 1. that the titanium oxide is amorphous and 2. that the value of hydration water is approximately $n = 4$. On the contrary, an hydrated titanium oxide, prepared by the same procedure crystallizes like anatase and has an approximate value of $n = 1$ [15].

The results of the thermogravimetric and the infrared spectroscopy confirmed the X-ray diffraction data. In the X-ray diagram we could see only a small crystallization of the brucite.

The DTA curve (Fig. 4) showed two endothermic peaks and one exothermic peak. The first endothermic peak was finished at 300 °C, and later the second endothermic peak $Tp = 380$ °C appears. These two endothermic peaks correspond to the peaks that we have observed in the DTG curves (Fig. 3) and confirm the thermogravimetric results.

At about 500 °C, an exothermic phenomenon began, which gave rise to a symmetrical peak of great intensity that finished at 650 °C. From 650 °C until 1000 °C no phenomena were observed.

If the DTA curve is obtained in a dynamic atmosphere, the endothermic and exothermic phenomena take place at lower temperatures (about 60 °C) than in a static atmosphere.

The analysis by X-ray powder diffraction of samples taken at pre-determined points of the DTA curve allows us to establish the transformations taking place in the sample during heating. The X-ray diagram of the sample taken at 300 °C (Fig. 1b) is identical to the initial sample (Fig. 1a): the loss of the hydration water does not produce changes in the crystalline structure of the precipitate. The X-ray diagram of the sample taken at 460 °C (Fig. 1c), shows that the sample is practically amorphous, with a slight suggestion of periclase.

Fig. 1d shows the X-ray diagram of the sample taken at the end of the exothermic peak, 660 °C, corresponding to the geikielite, $MgTiO_3$, which crystallizes in the hexagonal system. A release of calorific power, indicated by the exothermic peak in the DTA curve, accompanies the formation of geikielite. The X-ray diagram of a sample heated to 600 °C in a dynamic atmosphere is that shown in Fig. 1d.

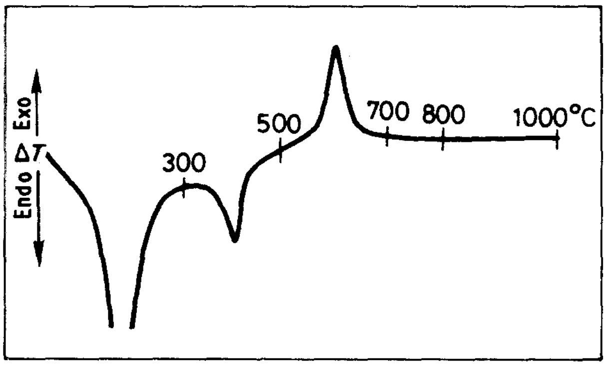

Figure 4 DTA curve of the precipitate.

Fig. 2b shows the i.r. spectrum of the geikielite at 600 °C. This spectrum coincides with that given by Baran and Botto [16].

The X-ray diagram of the sample taken at 1000 °C is showed in Fig. 1e. As we can observe in the X-ray diagram, the rise in temperature only produces an improvement of the crystalline system.

All the residues of calcination were analysed with an energy dispersive spectrometer (Kevex 7077). The analysis indicated that the composition of all of them is Ti/Mg 1/1 M.

These last results show that this method of coprecipitation provides materials perfectly homogeneous with reproducible stoichiometry and purity of particles.

As the magnesium titanate, $MgTiO_3$, geikielite, has many applications in the dielectric ceramics field, we made measures of the dielectric constant (ε) and the electric resistivity (ρ).

These measures were carried out from a tablet of about 80 mg, sintered at 1350 °C in an oven for 4 hours. The sintered tablet had a diameter of 5.0 mm and a thickness of 1.0 mm. These measures were made at room temperature and 1 KHz of frequency.

The value of the dielectric constant was 15.0 and the value of the electric resistivity was $1.1 \times 10^{10}\ \Omega.\text{cm}^{-1}$, these values are similar to values found in the literature.

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